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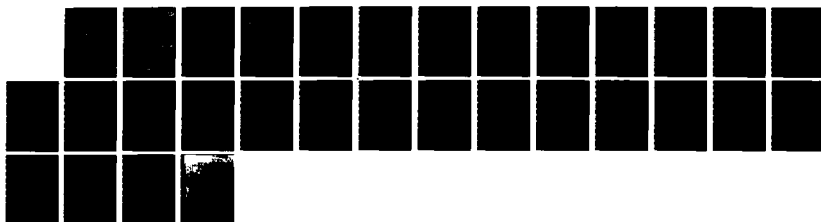
CRACK HEALING IN POLYMERS(U) ILLINOIS UNIV AT URBANA
DEPT OF METALLURGY AND MINING ENGINEERING R P WOOL
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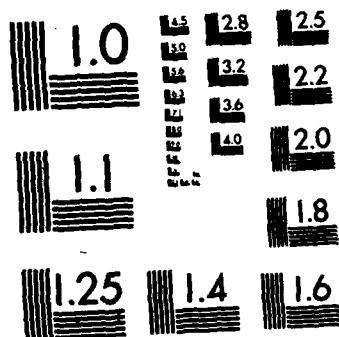
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20. ABSTRACT CONTINUED

Abstract

The healing of cracks, crazes, voids and mechanical energy losses were studied in a variety of polymer materials. These included amorphous, crystalline, crosslinked polymers, block copolymers and both rigid and soft composites. Mechanical testing methods consisted of uniaxial tension, wedge cleavage, compact tension, fracture, lap shear joint fracture, single edge notch fracture, Izod impact and compact tension fatigue. The important problem to solve was that of strength development, σ , at a polymer-polymer interface as a function of time, t , temperature, T , pressure, P , and molecular weight, M . Solutions were obtained in terms of the static and dynamic properties of random coil amorphous polymer chains as, $\sigma \sim t^{1/4} M^{-1/4}$ and the virgin state as, $\sigma_{\infty} \sim M^{1/2}$. The critical fracture energy, G_{IC} , behaved as $G_{IC} \sim t^{1/2} M^{-1/2}$ and $G_{IC}(\infty) \sim M$ for a wide molecular weight range. The healing (or processing) time, t_{∞} , behaves as $t_{\infty} \sim M^3 \exp P/T$. The self-diffusion coefficient, D , is measured mechanically from healing studies as $D = A/M^2$. The crack propagation rate, da/dN , in fatigue, behaves as $da/dN \sim M^{-5/2}$ and for fatigue healing, $da/dN \sim t^{-5/4} M^{5/4}$. These relations have been shown to apply to related problems, such as, tack and green strength of elastomers, lamination and powder processing, and provide a molecular basis for understanding fracture mechanics of linear polymers. The results are summarized and described in detail in 30 ARO related presentations and publications.

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Crack Healing in Polymers

by

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Crack Healing in Polymers

Introduction

In recent years, we have examined the rate of healing of cracks, voids, crazes and interfaces in a variety of materials. The understanding of strength development at a polymer-polymer interface in terms of the molecular dynamics and spatial configuration of the polymer chains also provides solutions to many related problems. These include welding, processing, molding, fatigue, fracture, tack, green strength, adhesion, lamination, coatings, etc. The results of this study are contained in the first 30 entries of the bibliography and this report mainly summarizes our approach to the problem and a list of important results.

Statement of Problem

The most fundamental healing problem is as follows: When two polymer solids of molecular weight M are brought into good contact at temperature T and hydrostatic pressure P , how do the fracture stress σ and fracture energy G_{IC} increase with contact time, t .

The problem is considerably simplified by assuming (i) instant molecular contact (wetting) of the interface, (ii) both polymers are composed of equal monodisperse molecular weight distributions and (iii) the polymer chains are linear and obey random-coil statistics. Deviations from these assumptions have been treated also.

Approach to a Solution

A solution to the healing problem is approached by first considering the molecular aspects of the problem in terms of the dynamics of random-coil chains in the bulk. This permits the determination of interdiffusion distances, number of bridges crossing the interface, etc. in terms of time and molecular weight, and provides a molecular description of the interface. Secondly, we consider a microstructural fracture criterion which relates local

macroscopic stresses to the molecular configuration at the interface in a small volume element using a known stress field independently of stress concentrations. Finally, using the microstructural fracture criteria we compute the fracture energy, G_{IC} , for a crack with a nonuniform stress field near the crack tip using the linear-elastic fracture mechanics (LEFM) approximation. The above three components to the solution of the crack/interface healing problem are presented in the following sections.

Molecular Aspects of Crack Healing

1. Molecular Dynamics of Random-Coil Chains:

The reptation model of deGennes [31] provides a useful description of the motion of polymer chains in an entangled melt and leads to the following important relations:

$$\langle l^2 \rangle = 2D_r t \quad (1)$$

$$D_r \sim M^{-1} \quad (2)$$

$$\langle x^2 \rangle \sim \langle l^2 \rangle^{1/2} \quad (3)$$

$$\langle x_{cm}^2 \rangle = 2Dt \quad (4)$$

$$D \sim M^{-2} \quad (5)$$

$$t_{\infty} \sim M^3 \quad (6)$$

in which $\langle l^2 \rangle$ is the mean square curvilinear path diffused by a single chain along its tube of topological constraints; D_r is the one-dimensional reptation diffusion coefficient which is inversely proportional to molecular weight, M ; t is the diffusion time which is equivalent to contact time in the healing problem; $\langle x^2 \rangle$ is the mean square monomer segment displacement distance; $\langle x_{cm}^2 \rangle$ is the mean square center-of-mass displacement; t_{∞} is the time required for the chain to renew its conformation, or, relax (escape) from its original "tube"; t_{∞} is also known as the reptation time and in crack healing, corresponds to the time required to achieve complete healing.

2. Number of Chains Intersecting Interface $n(t)$:

The number of random-coil chains intersecting unit area of the interface as a function of contact time t , and molecular weight, M , is obtained as

$$n(t) \sim t^{1/4} M^{-5/4} \quad (t < t_{\infty}) \quad (7)$$

$$n_{\infty} \sim M^{-1/2} \quad (t > t_{\infty}) \quad (8)$$

Note that Eq. (7) refers to the healing problem and Eq. (8) provides the solution for the virgin state. This is one of the major benefits of this analysis, i.e. that the virgin state represents one point or the static equilibrium solution (at $t = t_{\infty}$) on the healing equation.

3. Number of Bridges Intersecting Interface, $p(t)$:

Each time a piece of chain crosses back and forth through the interface, it creates a molecular bridge. The number of such bridges intersecting unit area of interface is obtained as

$$p(t) \sim t^{1/2} M^{-3/2} \quad (9)$$

$$p_{\infty} \sim M^0 \quad (10)$$

Note that the number of bridges in the virgin state is independent of molecular weight. Eq. (10) is obtained from Eq. (9) by substituting $t_{\infty} \sim M^3$ in Eq. (9).

4. Average Interpenetration Length, $l(t)$:

The average curvilinear length of chain segments which have self-diffused across the interface is obtained as

$$l(t) \sim t^{1/2} M^{-1/2} \quad (11)$$

$$l_{\infty} \sim M \quad (12)$$

and

$$\phi(l) \sim l^{-3/2}$$

where $\phi(l)$ is the distribution function for the number of interpenetrated segments of length l .

We will see later that this quantity is most critical for determining mechanical properties. $l(t)$ also corresponds to the minor chain length [23] which has diffused from its original tube.

5. Total Interpenetration Length, $l_0(t)$:

Depending on their distance from the interface at $t = 0$, individual chains will have interdiffused by different amounts. The total interdiffusion lengths of all the chains per unit area is obtained as

$$l_0(t) \sim t^{3/4} M^{-7/4} \quad (13)$$

$$l_0(\infty) \sim M^{1/2} \quad (14)$$

6. Average Interpenetration Depth, $X(t)$:

The interpenetration depth of monomer segments on interdiffusing chains behaves as

$$X(t) \sim t^{1/4} M^{-1/4} \quad (15)$$

$$X_{\infty} \sim M^{1/2} \quad (16)$$

These equations also describe the motion of the chain ends and the motion of a single monomer on the chain. Note that when $t > t_{\infty}$, the monomer motion is similar to the center of mass motion of the chain.

7. Total Interpenetration Depth, $X_0(t)$

Summing over all the interpenetration depths per unit area of the interface, the total interpenetration depth of chain segments is obtained as

$$X_0(t) \sim t^{1/2} M^{-3/2} \quad (17)$$

$$X_{0\infty} \sim M^0 \quad (18)$$

8. Average Length of Bridge, $l_p(t)$:

The average length of a molecular bridge across the interface is determined as

$$l_p(t) \sim t^{1/4} M^{-1/4} \quad (19)$$

$$l_{p\infty} \sim M^{1/2} \quad (20)$$

9. Number of Broken Bonds at Fracture, N_c :

The number of broken bonds at fracture is determined from molecular weight studies of fractured or sliced surfaces according to

$$M = \frac{M_0}{1 + M_0^x} \quad (21)$$

where M_0 is the virgin initial molecular weight and x is determined by

$$N_c \sim M_0^x \quad (22)$$

Recent fracture experiments with monodisperse polystyrene using GPC analysis [30] indicate that $x \approx 1/2$ suggesting that since $N_c \sim M^{1/2}$ that N_c is controlled by either (i) the average length of a bridge $l_{p\infty}$, (ii) the average interpenetration depth x_∞ or (iii) the total interpenetration length, $l_{0\infty}$. This problem is being pursued.

In the next section we examine how the above molecular aspects of the problem contribute to the mechanical properties of the interface.

Microstructural Fracture Criteria

A strain energy approach to fracture was adopted which considers both chain pull-out and chain fracture mechanisms at the interface. Consider a

a volume element containing a small area of interface. A uniaxial stress, σ , is acting normal to the interface such that the strain energy density, U , of the volume element is given in the linear elastic manner as

$$U = \frac{\sigma^2}{2Y} \quad (23)$$

where Y is the tensile Young's modulus of the volume element. We have shown experimentally and theoretically that

$$Y \sim t^0 M^0 \quad (24)$$

$$Y_\infty \sim M^0 \quad (25)$$

such that Y remains constant during healing and fracture.

The number of chains per unit volume, N_v , is

$$N_v = \frac{\rho N_a}{M} \quad (26)$$

where ρ is the density and N_a is Avogadro's number. The strain energy density per chain, U_c , is therefore obtained as

$$U_c = U/N_v = \frac{\sigma^2 M}{2Y \rho N_a} \quad (27)$$

Since $l \sim M$, the strain energy associated with a (segment of) chain of length l is in this case,

$$U_c \sim \sigma^2 l \quad (28)$$

The stored strain energy in the chain can be used to either fracture the chain or pull it out across the interface when fracture occurs. A fracture criterion for chain pull-out can be written as

$$U_c > U_p \quad (29)$$

where U_p is the energy to pull a chain out of its tube. U_p is calculated using the force $f = \mu_0 l \, dl/dt$, from the integral of $f dl$, as

$$U_p = \int \mu_0 l \left(\frac{dl}{dt} \right) dl \quad (30)$$

where μ_0 is the monomer friction coefficient and dl/dt is a constant pull-out rate. Thus

$$U_p = \frac{1}{2} \mu_0 \frac{dl}{dt} l^2 \quad (31)$$

or

$$U_p \sim l^2$$

A similar result is obtained if the chain is pulled out at constant force. Equating Eq. (28) with (31) as in Eq. (29), we obtain

$$\sigma \sim \sqrt{l} \quad (32)$$

or

$$\sigma \sim X \quad (33)$$

where X is the average interpenetration distance. Thus the fracture stress in uniaxial tension in the absence of a large stress concentration factor should behave as

$$\sigma \sim t^{1/4} M^{-1/4} \quad (34)$$

and

$$\sigma_{\infty} \sim M^{1/2} \quad (35)$$

with a strain rate, $\dot{\epsilon}$, dependence of $\sigma \sim \dot{\epsilon}^{1/2}$. The stored energy U_C at fracture behaves as

$$U_C \sim t^{1/2} M^{-1/2} \quad (36)$$

and

$$U_{C\infty} \sim M \quad (37)$$

By examining Eq. (31), one sees that fracture by the chain pull-out mechanism is favored at low molecular weight (small l) low deformation rates (small dl/dt), high temperatures (low μ_0) and short healing times (small t). When the energy to pull a chain out exceeds the bond rupture energy of that chain, the chain or chain segment breaks. In the bond rupture mechanism, if the number of bridges $p(t)$ crossing the interface becomes the controlling molecular factor then the fracture energy and stress are obtained as

$$U_C \sim t^{1/2} M^{-3/2} \quad (38)$$

$$U_{C\infty} \sim M^0 \quad (39)$$

$$\sigma \sim t^{1/4} M^{-3/4} \quad (40)$$

$$\sigma_{\infty} \sim M^0 \quad (41)$$

Note that σ still follows the $t^{1/4}$ law but that the molecular weight dependence of both the healing slope and the virgin state is different than the chain pull-out result. The latter differences can be used to identify the dominant mechanism in a particular fracture case. Chain fracture is favored at low

temperature, fast testing rate, high molecular weights and long healing times. In most fracture cases, mixed mechanisms will occur and the contribution of each mechanism is currently being evaluated using distribution functions for interpretation lengths and bridges coupled with a GPC analysis of bond rupture as a function of molecular weight and temperature.

In the next section, we examine a fracture mechanics model which can be used to relate the above microstructural fracture model to the critical strain energy release rate, G_{IC} , for a cracked body.

Fracture Mechanics

The Dugdale model [32] was used to analyze the molecular aspects of fracture mechanics. In this model, a crack of length a_0 propagates through a plastic line-zone or craze of length r_p ahead of the crack tip. The stress field near the crack for a cartesian volume element xyz and angle θ at distance r is given by Rice [33] as

$$\begin{aligned}\sigma_x &= \frac{K_1}{\sqrt{2r}} \cos \frac{\theta}{2} \left[1 - \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \dots \\ \sigma_y &= \frac{K_1}{\sqrt{2r}} \cos \frac{\theta}{2} \left[1 + \sin \frac{\theta}{2} \sin \frac{3\theta}{2} \right] + \dots \\ \sigma_{xy} &= \frac{K_1}{\sqrt{2r}} \cos \frac{\theta}{2} + \dots\end{aligned}\tag{42}$$

where K_1 is the stress intensity factor. The length of the plastic zone is determined by

$$r_p = \frac{\pi}{8} \frac{K_1^2}{\sigma_c^2}\tag{43}$$

where σ_c is the critical stress to initiate fracture. The critical crack opening displacement is given by

$$\delta^* = \frac{k_1^2}{\sigma_c Y} \quad (44)$$

where Y is the modulus corrected for plane stress or plane strain.

For the case where σ_c is constant within the plastic zone, the critical strain energy release rate, G_{IC} , is determined by

$$G_{IC} = \int_0^{\delta^*} \sigma_c(\delta) d\delta$$

or,

$$G_{IC} = \sigma_c \delta^* \quad (45)$$

To evaluate the molecular aspects of the problem we first calculate σ_c using Eq. (27), such that the stored energy per molecule is

$$U_c = \frac{1}{N_v} \left(\frac{\sigma_x^2}{2Y} + \frac{\sigma_y^2}{2Y} + \frac{1}{2G} \sigma_{xy}^2 \right) \quad (46)$$

where G is the shear modulus. Substituting for σ_x , σ_y and σ_z at $\theta = 0$, U_c is dominated by the σ_y term, and as before

$$U_c \sim \sigma_y^2 l \quad (47)$$

Using the same criteria for chain pull-out Eq. (29) and letting $\sigma_y = \sigma_c$ at critical conditions, then

$$\sigma_c \sim \sqrt{l} \quad (48)$$

where l is the average interpretation length. The critical crack opening displacement is proportional to σ_c and thus [34,35]

$$\delta^* \sim \sqrt{l} \quad (49)$$

Substituting for σ_c and δ^* , G_{IC} is determined as

$$G_{IC} \sim t^{1/2} M^{-1/2} \quad (50)$$

$$G_{IC}(\infty) \sim M \quad (51)$$

The length of the plastic zone is determined for $K < K_{IC}$ from Eq. (43) as,

$$r_p \sim \frac{K^2}{T} \quad (52)$$

which suggests that at $K = K_{IC}$

$$r_p^* \sim M^0 \quad (53)$$

However the craze fibrillar lifetime in a propagating crack system should affect the observed craze length ahead of the crack. For subcritical crack propagation the observed craze length r' , should behave approximately as

$$r' = r_p \frac{t_p}{t_0} \quad (54)$$

where t_p is the time required to pull out the chains to cause fracture and t_0 is time required for the applied load to reach critical conditions such that when $t_p > t_0$, $r' = r_p^*$, and when $t_p < t_0$, $r' < r_p$.

The time to pull out a chain of length l is a useful quantity, particularly for fatigue and can be determined from $f = \mu_0 l \, dl/dt$, used in Eq. (30), as

$$t_p \approx \int \frac{\mu_0 l}{f} \, dl \quad (55)$$

The constant force f is proportional to σ_c in the craze zone in this case and it follows that

$$t_p \sim \frac{\mu_0 l^2}{\sigma_c} \quad (56)$$

or

$$t_p \sim l^{3/2} \quad (57)$$

Substituting for Eq. (51) and Eq. (52) in Eq. (54) the observed craze length, r' , ahead of a stable crack should be approximately described by

$$r' \sim l^{1/2} \quad (58)$$

or for virgin polymer glasses

$$r' \sim M^{1/2} \quad (59)$$

The most critical result from the Dugdale model analysis is $G_{IC} \sim 1$.

Fatigue

For similar crack systems as analyzed for the Dugdale model in the last section, we would like to evaluate the incremental crack advance per cycle, da/dN , at constant ΔK for a cyclically fatigued sample. The molecular aspects of the problem can be derived by considering the incremental increase in the plastic zone per cycle and the time required to pull chains out to allow the zone to propagate. The following approximation is made;

$$\left(\frac{da}{dN}\right)_{\Delta K} \sim \frac{r_p}{t_p} \quad (60)$$

Since $r_p \sim l^{-1}$ for $K < K_{IC}$ and $t_p \sim l^{3/2}$, it follows that

$$\frac{da}{dN} \sim \gamma^{-5/2} \quad (61)$$

During healing, we obtain

$$\frac{da}{dN} \sim t^{-5/4} M^{5/4} \quad (62)$$

and in the virgin state, it follows that

$$\frac{da}{dN} \sim M^{-5/2} \quad (63)$$

Relations for healing, fracture and fatigue with regard to chain pull-out and chain fracture mechanisms are summarized in Table 1.

Self-Diffusion

Crack healing provides another method of measuring self-diffusion coefficients, D , for polymer chains in the bulk since the chain moves a distance roughly equal to its radius of gyration as the mechanical properties, σ , K_{IC} or G_{IC} increase from zero to a maximum value. The self-diffusion coefficient is derived from the following relations for random coil chains consisting of N monomers of step length b and characteristic ratio, C_{∞} . The end-to-end vector, $\langle R^2 \rangle$, is given by

$$\langle R^2 \rangle = C_{\infty} N b^2 \quad (64)$$

At $t = t_{\infty}$, the curvilinear one dimensional diffusion length, L , is given by

$$\langle L^2 \rangle = 2D_r t_{\infty} \quad (65)$$

similar to Eq. (1). The center of mass motion is related to the end-to-end

vector, R and can be expressed by

$$\langle R^2 \rangle = 6Dt_{\infty} \quad (66)$$

Since $L = Nb$, we can solve the last three equations for D and obtain

$$D = D_r C_{\infty} M_0 / 3M \quad (67)$$

where $M_0 = M/N$ is the monomer molecular weight. D_r is obtained from healing studies as

$$D_r = \frac{1}{2} \left(\frac{k_2}{k_1} \right)^4 \left(\frac{b}{M_0} \right)^2 \quad (68)$$

where k_2 is the slope of K_{IC} vs. $t^{1/4}$ and k_1 is the slope of $K_{IC}(\infty)$ vs. $M^{1/2}$. Inserting for the hydrostatic pressure, P , dependence of the reptation diffusion coefficient, D is obtained finally in terms of T, P and M as

$$D(T, P, M) = \frac{C_{\infty} D_0 M_0}{3M^2} \exp - (Q_d + P\Delta V) / kT \quad (69)$$

where D_0 is a known constant, Q_d is the activation energy for diffusion (possibly temperature dependent in a WLF sense) and ΔV is an activation volume for the pressure dependence of diffusion, which can be estimated from the pressure dependence of the glass transition temperature, T_g . Eq. (69) was formulated for healing systems which are dominated by the chain pull-out mechanism. A similar expression could be derived for systems subject to chain fracture control but would have additional constants. The equation for D above only requires the experimental measurement of k_1 and k_2 .

Processing

When processing polymer resin and powder via injection or compression molding, the time, t_{∞} , to achieve complete equilibrium is readily obtained as a function of T , P and M as

$$t_{\infty}(T,P,M) = M^3 \left[\frac{b^2 \exp(Q_d + P\Delta V)/kT}{2M_0^2 D_0} \right] \quad (70)$$

For powder and pellets, the hydrostatic pressure, P accommodates the compaction and initial wetting at the interface prior to diffusion, but retards the interdiffusion process. Diffusion slows down with increasing P since the volume available to accommodate the "hopping" of molecules is reduced accordingly. The loss of mobility with increasing pressure also results in an increase in T_g . Note that $t_{\infty} \sim M^3$ in accordance with reptation theory.

Summary

Strength development at a polymer-polymer interface was analyzed as a function of time, temperature, pressure and molecular weight. Solutions were obtained in terms of the dynamics and statics of random coil chains. An understanding of the crack healing problem also provides solutions to related problems such as the molecular weight dependence of G_{IC} , fatigue, adhesion, processing, tack and green strength. We also used the interdiffusion process to provide a new method of measuring self-diffusion coefficients of polymer chains in the melt. Those relations are summarized in Table 1. Considerable experimental support exists for these scaling relations. A few important cases are as follows. Using cleavage-wedge methods with monodisperse polystyrene surfaces at the interface [36], our fracture tests show that $K_{IC} \sim t^{1/4} M^{-x}$ and $G_{IC} \sim t^{1/2} M^{-2x}$ where $x \approx 1/4$ for the molecular weight range $50,000 < M < 200,000$. In the same molecular weight range, the virgin state is described by $K_{IC} \sim M^{1/2}$

and $G_{IC} \sim M$. Kausch (37,38) has shown that for PMMA, $K_{IC} \sim t^{1/4}$ using compact tension specimens, but did not examine the molecular weight dependence of healing. Similar studies by our group on PMMA in a limited M -range indicated that $K_{IC} \sim t^{1/4} M^{-x}$ where again $x \leq 1/4$. These experiments are complicated by the altered molecular weight distribution due to molecular fracture in the healing interface. This problem is solved by using the cleavage wedge method with surfaces of known molecular weight distribution. Cleavage-wedge experiments of Robertson [39] on monodisperse low molecular weight ($M < M_c$) polystyrene also show that $G_{IC} \sim M$. Experiments by Ward [40] on polycarbonate using compact tension samples clearly show that $G_{IC} \sim M$ for many samples in the range $4000 < M < 10,000$. Using the Dugdale model, Ward also determined the craze stress, σ_c , which behaves approximately as $\sigma_c \sim M^{1/2}$. The critical crack opening displacement behaved approximately as $\delta \sim M^x$ where $1/2 < x < 1$ and the craze length, r_p , behaved as $r_p \sim M^x$ where $x \approx 1/2$ and M is the number average molecular weight. Ward's results are in remarkably good agreement with our predictions based on the Dugdale model. Prentice [41] recently analyzed the molecular weight dependence of G_{IC} using $G_{IC} \sim nU_p$ where n is the number of chains crossing the interface and U_p is the energy to pull chains out. He correctly lets $U_p \sim M^2$ but lets $n \sim M^0$ (actually $n \sim M^{-1/2}$) such that $G_{IC} \sim M^2$. Using Ward's data for polycarbonate as discussed above, he shows that $\log G_{IC}$ vs. $\log M$ has a slope of 2.5 in close agreement with his prediction. This is an artifact of the log-log plot arising from the fact that if one has a function, $y = x^n + c$ where c is a constant additive front factor, the slope n' of $\log y$ versus $\log x$ behaves as $n' > n$ if $c < 0$ and $n' < n$ if $c > 0$. For processing of pellet resin, our analysis of McCormick's data [42] shows that the fracture stress, σ_∞ , and fracture strain, ϵ_∞ , of both compression molded polystyrene plates and injection molded tensile coupons behaves as $\sigma_\infty \sim M^{1/2}$ and $\epsilon_\infty \sim M^{1/2}$ in the range $30,000 < M < 160,000$ for both monodisperse and polydisperse samples. The tensile impact energy, E_∞ , also behaved as $E_\infty \sim M$ in this

range. Our experiments with compression molded PS plates also show that $\sigma \sim t^{1/4}$ using similar pellet resin. The fatigue prediction that $da/dN \sim M^{-5/2}$ is remarkably well supported by data of Hertzberg [43] obtained with PVC and PMMA. Our studies of fatigue healing [44] using PS indicate that $da/dN \sim t^{-x}$ where x is approximately unity. The scaling predictions for fatigue are tentative, despite the good agreement and are being pursued both theoretically and experimentally. In particular we need to obtain da/dN for monodisperse molecular weight samples in both the virgin state and during healing. Unfortunately, the fatigue healing experiments are difficult to perform. Predictions for tack and green strength of uncured rubbery materials are very well supported by Forbes data [45]. The cohesive strength σ_{∞} , as a function of M behaves as $\sigma_{\infty} \sim M^{1/2}$ and the strength or tack at constant time for two contacted surfaces behaves as $\sigma \sim t^{1/4} M^{-1/4}$ in the range $M < 2.5 \times 10^6$ for reasonably monodisperse samples of natural rubber. The self-diffusion coefficient of natural rubber was calculated from Forbes' mechanical data using our healing theories, as $D = 1 \times 10^{-14}$ cm²/sec. Skewis [46], using tracer methods obtained $D = 3 \times 10^{-14}$ cm²/sec for natural rubber of unknown polydispersity. If the polydispersity of Skewis' sample used in the tracer experiment was 1.77, exact agreement would have been obtained. The strain rate, $\dot{\epsilon}$, dependence of the tack or green strength behaves exactly as $\sigma \sim \dot{\epsilon}^{1/2}$ as predicted in cases where chain pull-out dominates. With decreasing temperature, the cohesive failure stress becomes largely independent of $\dot{\epsilon}$ as chain fracture dominates. These results are in excellent agreement with recent data of Hamed [47] (although he uses a different interpretation of his own data) and with those of several other investigators).

Some of the theoretical predictions are also in agreement with other theories. Prager and Tirrell [48] and deGennes [49] have both predicted the number of bridges across the interface as $p(t) \sim t^{1/2} M^{-3/2}$ and $p_{\infty} \sim M^0$ in agreement with Eq. (9-10). However, we disagree with their assumption that

$G_{IC} \sim p(t)$ for all molecular weights, but this assumption may have some validity at very high molecular weights when $G_{IC} \sim M^0$. The theoretical results presented herein are for the symmetric monodisperse A/A interface. We can also analyze a variety of other symmetric A/A cases and asymmetric A/B pairs, where in the latter, polymer A is interdiffusing with polymer B. The next important A/A pair to consider is that for polydisperse samples of similar molecular weights. This study is in progress.

In conclusion, we have examined healing and fracture relations for monodisperse molecular weight amorphous polymers. However, we have conducted experiments on a variety of polymers to demonstrate that crack healing occurs. These include polydisperse molecular weight amorphous polymers, epoxies (Epon-828 type), semicrystalline polymers, block copolymers, lightly crosslinked rubbers, filled elastomers and asymmetric (A/B) pairs. In general, the recovery of a mechanical property z , normalized to that of the virgin state, behaves as

$$R(z, t) = \int_{\tau=-\infty}^{\tau=t} R_z^0(t-\tau) \frac{d\phi(\tau)}{d\tau} d\tau$$

where $R_z^0(t)$ is an intrinsic healing function and $\phi(t)$ is a wetting distribution function [9]. $R_z^0(t)$ is evaluated when $\phi(t)$ is a Dirac delta function, i.e., when instantaneous wetting of the crack interface occurs such that the time dependence of healing is now dependent on interdiffusion as in the amorphous chain case, or other mechanism such as primary bond reformation which may be important in epoxies. For partially wetted interfaces, the healing behavior becomes a convolution product of the intrinsic healing process with the time dependent wetting process and the simple scaling laws may become obscured. Thus, great experimental care must be taken when exploring healing relations to ensure that (close to) instantaneous wetting occurs at the interface.

Table 1

Summary Relations for Healing and Fracture

<u>Property</u>	<u>Relation</u>
$\sigma(t), K_{IC}(t)$	$t^{1/4}M^{-1/4}$ chain pull out (CPO) $t^{1/4}M^{-3/4}$ chain fracture (CF)
$\sigma_{\infty}, K_{IC\infty}$	$M^{1/2}$ (CPO) M^0 (CF)
$G_{IC}(t)$	$t^{1/2}M^{-1/2}$ (CPO) $t^{1/2}M^{-3/2}$ (CF)
$G_{IC}(\infty)$	M (CPO) M^0 (CF)
$\left(\frac{\partial a}{\partial N}\right)_{\Delta K}$	$t^{-5/4}M^{5/4}$ (CPO) $M^{-5/2}$ (CPO) M^0 (CF)
t_{∞}	$M^3 \exp P/T$
D	$M^{-2} \exp -P/T$

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